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ning of each regular issue of the PCT Gazette.*

(54) Title: NANOTUBES

(57) Abstract: The invention provides a nanotube coated with a metal sulphide, selenide or telluride at least 5% of the external surface of said nanotube being coated.



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Nanotubes

5 This invention relates to coated nanotubes, in particular to coated single or multi-walled carbon nanotubes and to new processes for the production thereof.

10 Carbon nanotubes, i.e. long, thin cylinders of carbon, were first discovered in 1991 when a Japanese researcher studied soot created in an electrical discharge between two carbon electrodes. These large macromolecules are of unique size, shape and possess valuable physical properties. They consist of one or more sheets of graphite rolled into concentric
15 cylinders.

These structures have engendered much interest in recent years and much research has been dedicated to their understanding. Studies of the physical properties of nanotubes are still in progress, and it is now agreed
20 that they exhibit a very broad range of electronic, thermal, and structural properties that depend on the different kinds of nanotube (defined by, for example, their diameter, length, and chirality). In view of the diverse properties of nanotubes, they have been proposed
25 for use in *inter alia* composite materials, actuators, atomic force microscope tips, nanoelectronic devices, super capacitors and quantum wires.

Specifically, previous research has demonstrated that nanotubes may exhibit high strength and high
30 resilience as well as being of potential interest in view of their electrical properties. Hence, nanotubes have been suggested for use in building materials as reinforcement agents or as solid lubricants. Perhaps more importantly, nanotubes are believed to have
35 applications in nanoscale electronic devices. It is envisaged that such devices may eventually replace silicon-based electronic technology.

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Nanotubes are, however, susceptible to oxidation and it would be useful if measures could be taken to prevent oxidation occurring. Also, nanotubes may exhibit metallic character and it would therefore be desirable to provide the tubes with a non-metallic, e.g. insulating or semi-conducting coating to allow further applications to be investigated. The coating of nanotubes with semiconducting materials is believed to be of particular interest in view of their special electrical properties.

Hsu *et al* in Applied Physics Letters, Vol. 77, No. 25, 18 December 2000 suggested coating a carbon nanotube with the semiconductors, molybdenum or tungsten disulphide.

Hsu *et al*'s process involves mixing air-oxidised carbon nanotubes with H_2MoO_4 or the corresponding tungsten compound in an aqueous alkali solution. After prolonged ultrasonication, filtering, washing and drying, the product is placed in a furnace at 950°C and exposed to a nitrogen/hydrogen sulphide mixture. However, as is clear from the publication, coating of the carbon nanotubes with the relevant disulphide is not achieved. Hsu *et al* report that the yield of carbon nanotubes efficiently coated with tungsten disulphide was very low: 0.5 to 1% from batch to batch. The report does not mention the formation of any molybdenum coated carbon nanotubes.

Thus, there still remains a need to create coated nanotubes efficiently and a process for the preparation of such nanotubes.

The applicants have surprisingly found that nanotubes coated with metal sulphide, selenide or telluride compounds can be produced if a metal oxide is deposited onto the surface of a nanotube and is subsequently converted into the desired coating material. Metal sulphides/selenides/tellurides can act as insulators, semiconductors or, in some cases,

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metallic conductors and hence the ability to successfully coat nanotubes with such species is desirable. Certain metal sulphides/selenides may also act as lubricants. The processes described below
5 therefore facilitate the preparation of such coated nanotubes, which are themselves new materials.

Thus, viewed from one aspect the invention provides a nanotube coated with a metal sulphide, selenide or telluride, preferably a semiconducting metal sulphide,
10 selenide or telluride, at least 5% of the external surface of said nanotube being coated.

Viewed from another aspect the invention provides a process for the preparation of a metal sulphide, selenide or telluride coated nanotube comprising heating
15 a metal oxide coated nanotube in hydrogen sulphide/selenide/telluride at conditions sufficient to convert said metal oxide into a metal sulphide/selenide/telluride.

Viewed from a further aspect the invention provides a process for the preparation of a metal sulphide, selenide or telluride coated nanotube comprising coating
20 a nanotube with a metal oxide and heating said metal oxide coated nanotube in hydrogen sulphide/selenide/telluride at conditions sufficient to
25 convert said metal oxide into a metal sulphide/selenide/telluride.

Viewed from a yet further aspect the invention provides a process for the preparation of a metal sulphide, selenide or telluride coated nanotube
30 comprising:

I) mixing a nanotube and a metal oxide precursor in an inert solvent;

II) evaporating the solvent to give a nanotube
35 coated with said metal oxide precursor;

III) subjecting said coated nanotube to conditions sufficient to convert the metal oxide precursor to said

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metal oxide;

IV) heating the product of step (III) in hydrogen sulphide/selenide/telluride at conditions sufficient to convert said metal oxide into a metal

5 sulphide/selenide/telluride.

Viewed from a still yet further aspect the invention provides a process for the preparation of a metal sulphide, selenide or telluride coated nanotube comprising:

10

I) dispersing a nanotube and a compound comprising a MO_4^{2-} ion in water;

II) bringing the dispersion into contact with an acid to precipitate $\text{MO}_3 \cdot x\text{H}_2\text{O}$;

15 III) isolating the nanotube coated with $\text{MO}_3 \cdot x\text{H}_2\text{O}$

IV) subjecting said nanotube to conditions sufficient to convert $\text{MO}_3 \cdot x\text{H}_2\text{O}$ to MO_3 ;

V) heating the product of step (IV) in hydrogen sulphide/selenide/telluride at conditions sufficient to convert MO_3 into a metal sulphide/selenide/telluride;

20 wherein M represents a metal and x is 1 or 2.

It is envisaged that the coating procedures described herein will work for all nanotubes, for example, those made of silicon, gallium arsenide, indium phosphide, boron carbon nitride, as well as carbon
25 nanotubes. Nanotubes made from compounds of transition metals may also be coated, e.g. nanotubes made from tungsten disulphide or molybdenum disulphide, metal carbides, such as TaC, NbC, TiC. In the preferred case, the nanotubes should be straight. In a further
30 preferred embodiment, the nanotubes to be coated should be single-walled carbon nanotubes or multi-walled carbon nanotubes. In an especially preferred embodiment, the carbon nanotubes are multi-walled. Without wishing to
35 be limited by theory, it is believed that the greater diameter of the multi-walled nanotubes aids the coating process since the coating is thought to form more easily

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around the bulkier multi-walled nanotubes. From hereon, the term "carbon nanotube" is intended to encompass both single and multi-walled carbon nanotubes. Similarly, the term "nanotube" is intended to encompass both single and multi-walled nanotubes of any substance.

The nanotubes to be coated according to the invention are known and may be purchased from commercial suppliers or made using conventional techniques. For example single-walled carbon nanotubes may be prepared by arc-discharge of graphite rods doped with cobalt or nickel. Such single-walled carbon nanotubes may also be purchased from the Smalley Group, USA. Multi-walled carbon nanotubes can be efficiently grown by the catalytic decomposition of a gas that contains carbon, iron often being employed as the catalyst, eg. Grobert et al., Appl. Phys. Lett., **75**, 3363 (1999).

Where the nanotubes are single-walled, they may be between 2 to 10 nm, preferably 2 to 5 nm in diameter and 2 to 5 μm in length. Multi-walled nanotubes are bulkier, having diameters of 5 to 30 nm, preferably 10 to 20 nm, and lengths of 3 to 10 μm . Multi-walled carbon nanotubes conventionally have between 5 and 30 walls.

The coating material may be any suitable metal sulphide, selenide or telluride compound. However, in a preferred embodiment, the coating material should be a semiconducting metal sulphide, selenide or telluride compound. In a preferred embodiment the coating material is a sulphide or selenide, especially a sulphide. Suitable metal sulphides, selenides or tellurides are those based on the transition or lanthanide metals, especially those in groups 4, 5 and 6 of the periodic table of elements. Especially preferred are the semiconducting metal sulphides/selenides/tellurides formed with the metals zirconium, titanium, molybdenum and tungsten. Sulphide, selenide or telluride compounds of vanadium, niobium and tantalum may exhibit metallic conductivity and a nanotube coated

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with such a material may have diverse electronic applications. The metals molybdenum and most especially tungsten are particularly favoured.

5 The metals should be in a stable oxidation state which will of course vary depending on the nature of the metal. In general the 3+, 4+ and 6+ oxidation states are preferred. In a most preferred embodiment, the metal should be in the 4+ oxidation state forming therefore a disulphide, diselenide or ditelluride.
10 Hence, WS_2 and MoS_2 are especially preferred as coating materials.

The coating procedure gives rise to nanotubes which have a coating covering at least 5% of the external surface area of the nanotube. Preferably 20%, more
15 preferably 30%, especially 50% or more of the surface is coated. For some applications of the coated nanotubes 100% coverage is preferred. However, for applications in the electronics field, 60 to 90%, e.g. 60 to 70%, especially 70 to 80% coating coverage may be preferable,
20 or that which can more easily provide dissimilar regions on the nanotube surface thereby facilitating, for example, formation of junctions between dissimilar electrical property regions on the nanotube. At higher coating coverage percentages, it can be considered that
25 the coating material forms a cylindrical nanotube encompassing the core nanotube.

The coating may be laid down as a single layer or more preferably as a multi-layer. For example, each nanotube may have 1 to 20 layers, e.g. 2 to 15 layers,
30 of coating on its surface. A preferable number of layers is 2 to 5. Where a multi-layer coating is present, it can correspondingly be considered that the core nanotube is coated by a multi-walled nanotube formed from the coating material.

35 The number of coating layers on the nanotubes and the percentage surface coverage can be determined by various experimental techniques known in the art. A

particularly suitable method involves the use of transition electron microscopy (TEM), specifically, high resolution TEM (HRTEM). The chemical make up of the surface of the nanotubes can be analysed using an energy-dispersive X-ray probe (EDX). The use of these devices is routine in the art.

The inner coating layer is conveniently separated by 3 to 5 Å from the nanotube. Internal separation of the coating layers may also be 5 to 7 Å, depending on the type of layered metal sulphide, selenide or telluride.

The inventors have found that the coated nanotubes, which are the subject of the invention, can be prepared by two separate but similar processes. Both rely on the conversion of a metal oxide present on the nanotube surface into the corresponding metal sulphide, selenide or telluride. The inventors have however, devised two separate techniques for generating the required metal oxide coated nanotubes, although in both processes the preparative method relies on coating the nanotubes with a metal oxide precursor and subsequent conversion of that precursor to the metal oxide.

For simplicity and clarity, the two processes will be described separately below. Specific mention will be made of tungsten disulphide although persons skilled in the art will understand that the principles outlined in the following passages can generally facilitate preparation of a large variety of suitably coated nanotubes.

In the first process, standard nanotubes (prepared by conventional techniques) are mixed with a metal oxide precursor, e.g. tungstic acid (H_2WO_4) which itself may be considered as a tungsten trioxide precursor, in an inert solvent. To ensure efficient mixing, standard techniques such as sonication may be employed. A metal oxide precursor, according to the invention, is a compound which can be readily converted into its

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corresponding metal oxide. By inert solvent, it is meant that the solvent does not react with either the nanotubes or the metal oxide precursor.

Suitable metal oxide precursors are of formula H_2MO_4 where M represents a metal ion, e.g. Mo, W. Other suitable precursors include compounds comprising MO_4^{2-} ions and metal isopolymetallates. In a preferred embodiment the metal oxide should be a precursor to a metal trioxide.

The nature of the inert solvent will depend on the nature of the nanotubes and metal oxide precursor. However, suitable inert solvents eg. liquid ammonia, may be used.

After the nanotubes have been mixed with the metal oxide precursor, e.g. tungstic acid, the inert solvent is conveniently removed by evaporation. This is achieved by any suitable means, e.g. for liquid ammonia the reaction mixture may simply be allowed to warm to room temperature. Organic solvents may be removed *in vacuo*.

The resulting solid is then exposed to conditions sufficient to convert the metal oxide precursor into the corresponding metal oxide, e.g. tungsten trioxide. The conditions required to convert various metal oxide precursors into their respective metal oxides will be readily determined by a skilled person. Where the metal oxide precursor is of formula H_2MO_4 the conversion may be achieved by heating the solid in an atmosphere containing oxygen at a temperature of 100°C or greater. The temperature employed should not however, be sufficient to cause oxidation of the nanotubes themselves. For carbon nanotubes therefore, it is preferable if the temperature is kept below 500°C. A suitable range is therefore 100°C to 500°C, especially 300 to 400°C, e.g. 350°C.

The oxygen containing atmosphere may conveniently be air. It is preferable if the oxygen containing

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atmosphere is made to flow over the nanotubes.

The resulting solid comprises a nanotube coated with metal oxide, e.g. tungsten trioxide. This intermediate species forms a further aspect of the invention. Thus, viewed from a yet further aspect, the invention provides a nanotube coated with a metal oxide, preferably metal trioxide, at least 5% of the external surface area of said nanotube being coated.

The metal oxide coated nanotube is then subjected to conditions sufficient to convert the metal oxide into the corresponding metal sulphide, selenide or telluride. Typically, this procedure involves heating the nanotube in the presence of hydrogen sulphide, hydrogen selenide or hydrogen telluride in an inert, non-oxidising atmosphere. A suitable heating temperature is in the range of 800°C to 1000°C, e.g. 900°C. The inert atmosphere is preferably provided by nitrogen which may be mixed with the hydrogen sulphide/selenide/telluride in a ratio of at least 3:1, preferably 5:1. Without wishing to be limited by theory it is believed that the presence of the nitrogen gas not only prevents oxidation of the nanotubes themselves, but also prevents the hydrogen gas given off during the process from reacting with partly oxidized nanotubes, which may form as a result of heating carbon nanotubes in air.

It is preferable if the nitrogen/hydrogen sulphide/selenide/telluride mixture flows over the nanotubes.

The method described above has been found to yield nanotubes having between 1 and 3 coating layers. In a typical coating procedure 50% to 80% of the nanotubes are coated. Of those which are coated, approximately 60 to 70% of the nanotube surface is coated. More coating layers and greater nanotube surface coverage can be achieved by repeating the process. Any non-coated nanotubes are also likely to become coated on repetition of the process.

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In a second coated nanotube preparation process, a metal oxide precursor material and the nanotubes are dispersed in a liquid medium, e.g. water, before the precursor is precipitated onto the nanotubes. Again, 5
sonication or the like may be employed to ensure excellent mixing. The precursor of choice in this method is a MO_4^{2-} salt where M again represents a metal as defined above.

On addition of acid, e.g. hydrochloric acid, MO_3 10
with one or two waters of crystallisation ($\text{MO}_3 \cdot 2\text{H}_2\text{O}$ or $\text{MO}_3 \cdot \text{H}_2\text{O}$) precipitates and coats the nanotubes. The acid must be strong enough to ensure that precipitation occurs but not too strong otherwise the nanotubes may be oxidised. A 2.0M solution is preferred. At ambient 15
temperature, treatment of the MO_4^{2-} species with the acid tends to yield a $\text{MO}_3 \cdot 2\text{H}_2\text{O}$ group although if the solution is warmed a single water of crystallisation may be found.

After precipitation the coated nanotubes are 20
isolated. This can be readily achieved by filtering the mixture, washing with the liquid medium and drying *in vacuo*.

It is then necessary to convert the metal oxide precursor into the metal oxide itself. This may be 25
achieved by heating the nanotubes in an atmosphere containing oxygen at a temperature of 100°C or greater. The temperature employed should not however, be sufficient to cause oxidation of the nanotubes themselves. For carbon nanotubes therefore, it is 30
preferable if the temperature is kept below 500°C . A suitable range is therefore 100°C to 500°C , especially 300 to 400°C , e.g. 350°C .

The oxygen containing atmosphere may conveniently be provided by air. It is preferable if the oxygen 35
containing atmosphere is made to flow over the nanotubes. After formation of the metal oxide, conversion into the metal sulphide, selenide or

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telluride can then be achieved as described previously.

This second production method tends to yield nanotubes coated with a greater number of layers, e.g. 5 to 15 layers. In a typical coating procedure 50% to 80% of the nanotubes are coated. Of those which are coated, approximately 60 to 70% of the nanotube surface is coated. More coating layers and greater nanotube surface coverage can again be achieved by repeating the process. Any non-coated nanotubes are also likely to become coated on repetition.

The above processes provide excellent control over the coating process, without the necessity for specialist equipment such as sputtering, chemical vapour deposition or lithographic equipment. The two processes simply require the chemicals and a furnace.

The nanotubes described in the invention have applications in a variety of fields of endeavour. For example, carbon nanotubes have a very high tensile strength (approximately 100 times that of steel weight for weight). For this reason, such nanotubes have been proposed for use as reinforcers in building materials and the like. In such an application, it will be desirable that the nanotubes should not deteriorate when exposed to the elements. Appropriate coating layers in accord with the present invention can act as protective layers, preventing any oxidation of nanotubes in air or moisture.

Carbon nanotubes are also known to act as solid lubricants. Semiconducting metal sulphides and selenides are also known to be solid lubricants and hence a combination of these two lubricants in the nanotubes of the invention may give rise to beneficial lubricating properties.

Perhaps the most important application of the nanotubes of the invention is believed to lie in the electronics industry. It is desirable to provide miniature electronic device components that have, for

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example, metallic, semi-conducting and/or insulating electrical properties. Appropriately coated nanotubes, in accordance with the present invention, can be designed so as to have such properties, either on a whole or in regions along their length (e.g. where they are partly coated). Such nanotubes could facilitate the manufacture of nanoscale electronic devices. Thus, nanotubes with an insulating coating may act as insulated wires to be used as connectors in microscale electronic devices. Nanotubes of the invention could also act as nanoscale switches and can be provided with dissimilar electronic junctions, e.g. between a semiconducting coated region and a metallic region, thereby facilitating the construction of electronic devices.

Thus viewed from yet another aspect the invention provides the use of a coated nanotube as hereinbefore described as a reinforcement agent, lubricant or in an electronic device.

It is envisaged that other materials may be used to coat nanotubes. For example, where a nanotube is being used as an insulator, it may be preferable to coat the tube with an insulating substance. Similarly, the coating of the nanotubes with lubricants and antioxidants is envisaged.

Viewed from another aspect therefore, the invention provides a nanotube wherein at least 5% of the external surface of said nanotube is coated by a semi-conducting, lubricating, antioxidant or insulating material.

The invention will now be described further with reference to the following Examples and Figures in which Figures 1 and 2 show multi-walled carbon nanotubes coated with WS_2 and Figure 3 shows a single-walled carbon nanotube bundle coated with WS_2 .

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Example 1**WS₂ coated multi-walled carbon nanotubes (MWCN'S)**

5 Arc-made MWCN's (50 mg) and H₂WO₄ (250 mg) were mixed in liquid ammonia (5 ml, -78°C). The mixture was continuously stirred and allowed to rise to room temperature so that the ammonia evaporated. The resulting solid was heated at 350°C for 30 mins under a
10 continuous flow of air (100 cm³/min). The resulting material was further heated at 900°C in a mixture of nitrogen and hydrogen sulphide gas (50 cm³/min, N₂/H₂S ratio 3:1) for ten minutes. The resulting nanotubes showed 1 to 3 layers of WS₂ partly coating (approx 60%)
15 the MWCN.

Example 2**WS₂ coated multi-walled carbon nanotubes (MWCN'S)**

20 Arc made MWCN's (50 mg) were ultrasonically dispersed in a solution of Na₂WO₄.2H₂O (250 mg) in deionised water. Ultrasonication was carried out for ten minutes. Hydrochloric acid (20 ml, 2.0 M) was then added to
25 precipitate WO₃.2H₂O. The mixture was filtered, washed with deionised water and dried under vacuum. The resulting solid was heated at 350°C for 30 mins under a continuous flow of air (100 cm³/min). The resulting material was further heated at 900°C in a mixture of
30 nitrogen and hydrogen sulphide gas (50 cm³/min, N₂/H₂S ratio 3:1) for ten minutes. The resulting nanotubes showed up to 15 layers of WS₂ partly coating (approx 60%) the MWCN's.

Example 3**WS₂ coated single-walled carbon nanotubes (SWCN'S)**

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Arc-made SWCN bundles (50 mg) and H_2WO_4 (250 mg) were mixed in liquid ammonia (5 ml, -78°C). The mixture was continuously stirred and allowed to rise to room temperature, so that the ammonia evaporated. The
5 resulting solid was heated at 350°C for 30 mins under a continuous flow of air ($100\text{ cm}^3/\text{min}$). The resulting material was further heated at 900°C in a mixture of nitrogen and hydrogen sulphide gas ($50\text{ cm}^3/\text{min}$, $\text{N}_2/\text{H}_2\text{S}$ ratio 3:1) for ten minutes. The resulting nanotubes
10 showed 8 to 12 layers of WS_2 , which fully coat the SWCN bundles. These structures are usually open at one end and closed at the other. The WS_2 nanotube coating may be up to $2\text{ }\mu\text{m}$ in length.

Claims

- 5 1. A nanotube coated with a metal sulphide, selenide
 or telluride at least 5% of the external surface of said
 nanotube being coated.
2. A nanotube as claimed in claim 1 wherein said
10 nanotube is a single-walled carbon nanotube or a multi-
 walled carbon nanotube.
3. A nanotube as claimed in claim 1 or 2 wherein said
 nanotube is coated with a metal sulphide or selenide.
- 15 4. A nanotube as claimed in any one of claims 1 to 3
 wherein said nanotube is coated with a zirconium,
 titanium, molybdenum or tungsten sulphide.
- 20 5. A nanotube as claimed in any one of claims 1 to 4
 wherein said nanotube is coated with WS_2 or MoS_2 .
6. A nanotube as claimed in any one of claims 1 to 5
 wherein 60 to 90% of the external surface of the
25 nanotube is coated.
7. A nanotube as claimed in any one of claims 1 to 6
 wherein the nanotube comprises 2 to 15 layers of coating
 on its surface.
- 30 8. A process for the preparation of a metal sulphide,
 selenide or telluride coated nanotube comprising heating
 a metal oxide coated nanotube in hydrogen
 sulphide/selenide/telluride at conditions sufficient to
35 convert said metal oxide into a metal
 sulphide/selenide/telluride.

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9. A process as claimed in claim 8, wherein said metal oxide coated nanotube is heated in the presence of hydrogen sulphide/selenide/telluride at a temperature of 800 to 1000°C.

5

10. A process as claimed in claim 9 wherein said heating step takes place in the presence of nitrogen.

10

11. A process as claimed in claim 10 wherein the ratio of nitrogen to hydrogen sulphide/selenide/telluride is about 5:1.

15

12. A process as claimed in any one of claims 8 to 11 wherein said metal oxide coated nanotube is prepared by:

I) mixing a nanotube and a metal oxide precursor in an inert solvent;

II) evaporating the solvent to give a nanotube coated with said metal oxide precursor;

20

III) subjecting said coated nanotube to conditions sufficient to convert the metal oxide precursor to said metal oxide.

25

13. A process as claimed in claim 12 wherein said metal oxide precursor is of formula H_2MO_4 wherein M represents a metal ion.

30

14. A process as claimed in claim 13 wherein said metal oxide precursor is H_2WO_4 or H_2MoO_4 .

35

15. A process as claimed in any one of claims 12 to 14 wherein said inert solvent is liquid ammonia.

16. A process as claimed in any one of claims 12 to 15, wherein said metal oxide precursor coated nanotube is heated in an atmosphere containing oxygen at a temperature of 100°C to 500°C.

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17. A process as claimed in claim 16, wherein said metal oxide coated nanotube is heated in the presence of oxygen at a temperature of 300 to 400°C.

5 18. A process as claimed in any one of claims 8 to 11 wherein said metal oxide coated nanotube is prepared by:

I) dispersing a nanotube and a compound comprising a MO_4^{2-} ion in water;

10 II) bringing the dispersion into contact with an acid to precipitate $\text{MO}_3 \cdot x\text{H}_2\text{O}$;

III) isolating the nanotube coated with $\text{MO}_3 \cdot x\text{H}_2\text{O}$

IV) subjecting said nanotube to conditions sufficient to convert $\text{MO}_3 \cdot x\text{H}_2\text{O}$ to MO_3 ;

15 wherein M represents a metal ion and x is 1 or 2.

19. A process as claimed in claim 18 wherein said MO_4^{2-} ion is WO_4^{2-} or MoO_4^{2-} .

20 20. A process as claimed in claim 18 or 19 wherein said acid is HCl.

21. A process as claimed in any one of claims 18 to 20 wherein said $\text{MO}_3 \cdot x\text{H}_2\text{O}$ coated nanotube is heated in an atmosphere containing oxygen at a temperature of 100°C to 500°C.

22. A process as claimed in claim 21 wherein said $\text{MO}_3 \cdot x\text{H}_2\text{O}$ coated nanotube is heated in an atmosphere containing oxygen at a temperature of 300 to 400°C.

23. A process as claimed in any one of claims 8 to 17 wherein said metal oxide is MO_3 wherein M represents a metal ion.

35

24. A nanotube coated with a metal oxide at least 5% of the external surface area of said nanotube being coated.

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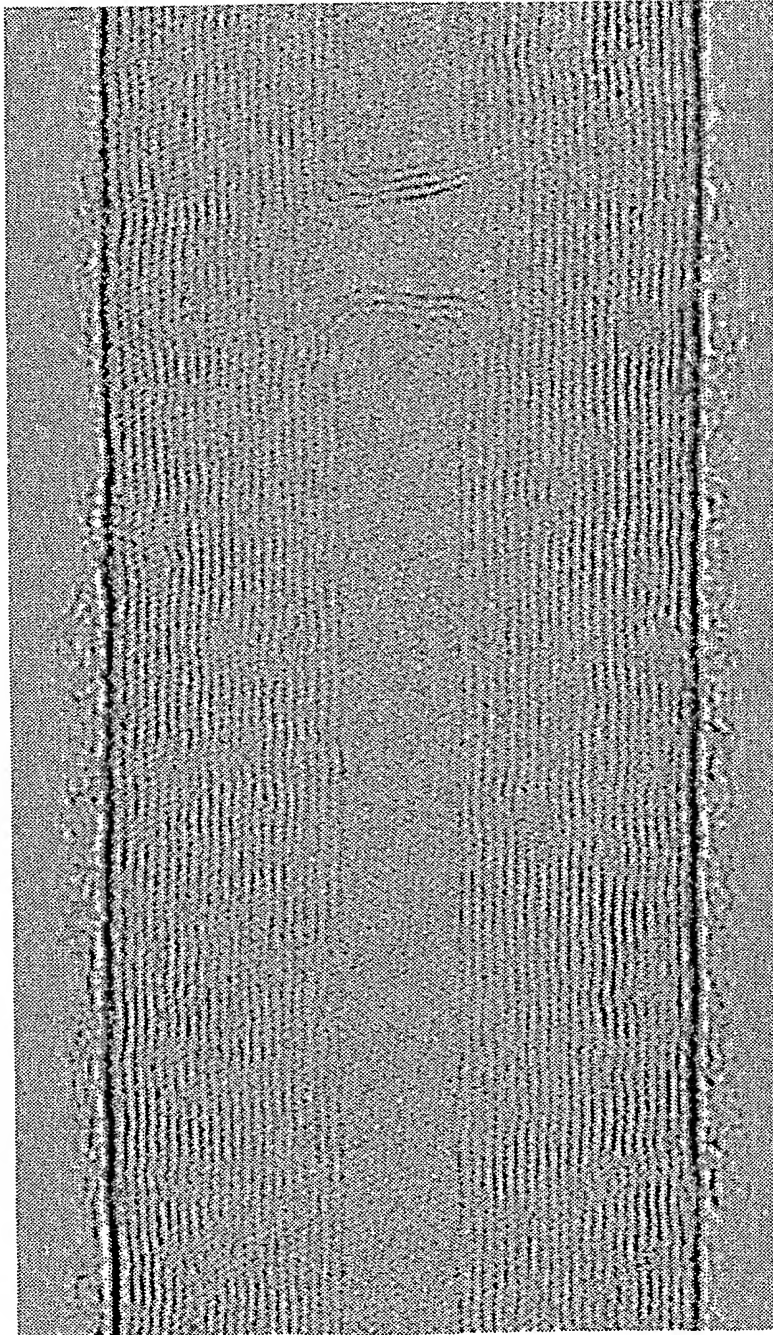
25. Use of a metal sulphide, selenide or telluride coated nanotube as claimed in any one of claims 1 to 7 as a reinforcement agent, lubricant or in an electronic device.

5

26. A nanotube wherein at least 5% of the external surface of said nanotube is coated by a semi-conducting, lubricating, antioxidant or insulating material.

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Figure 1



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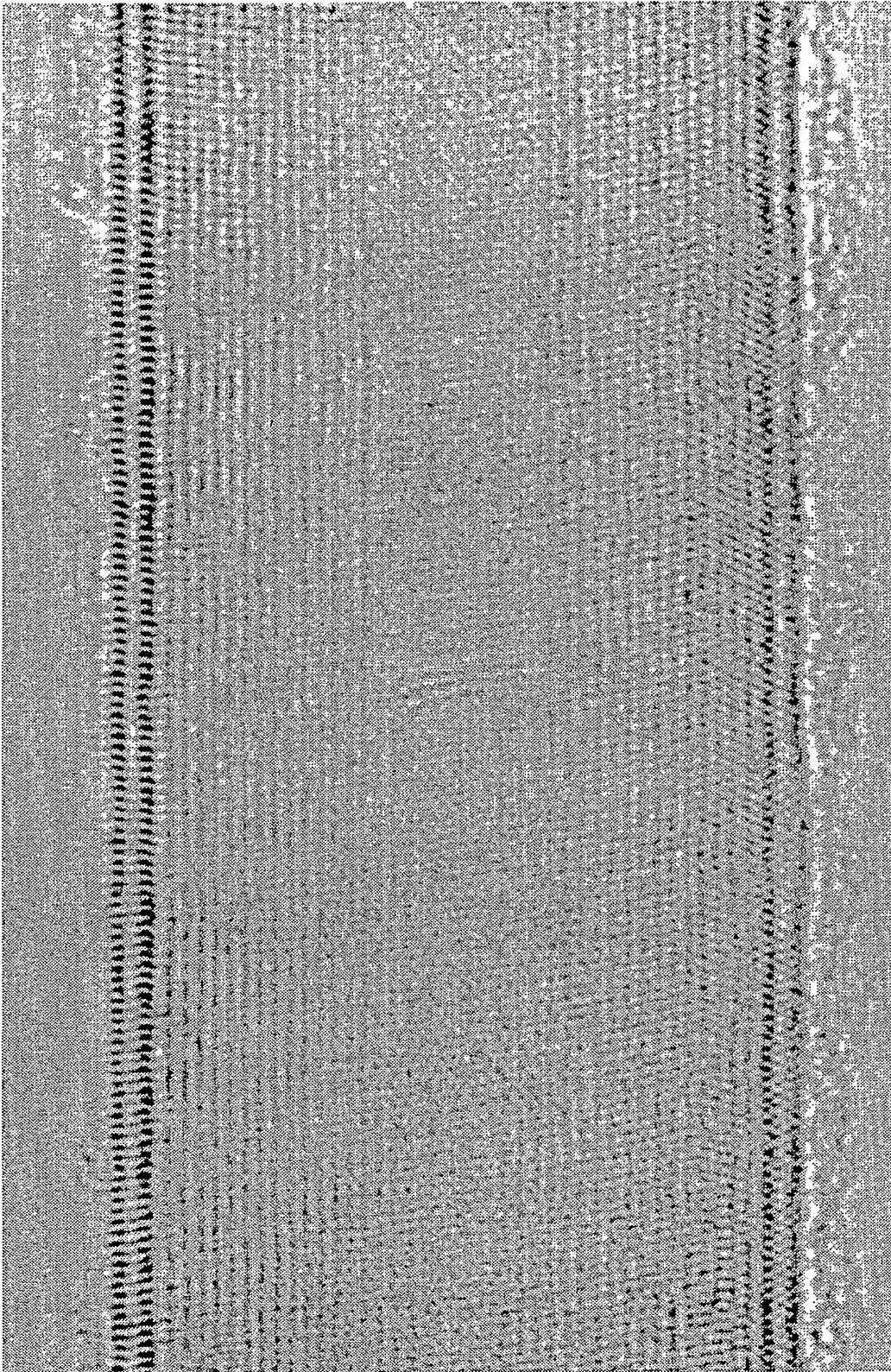
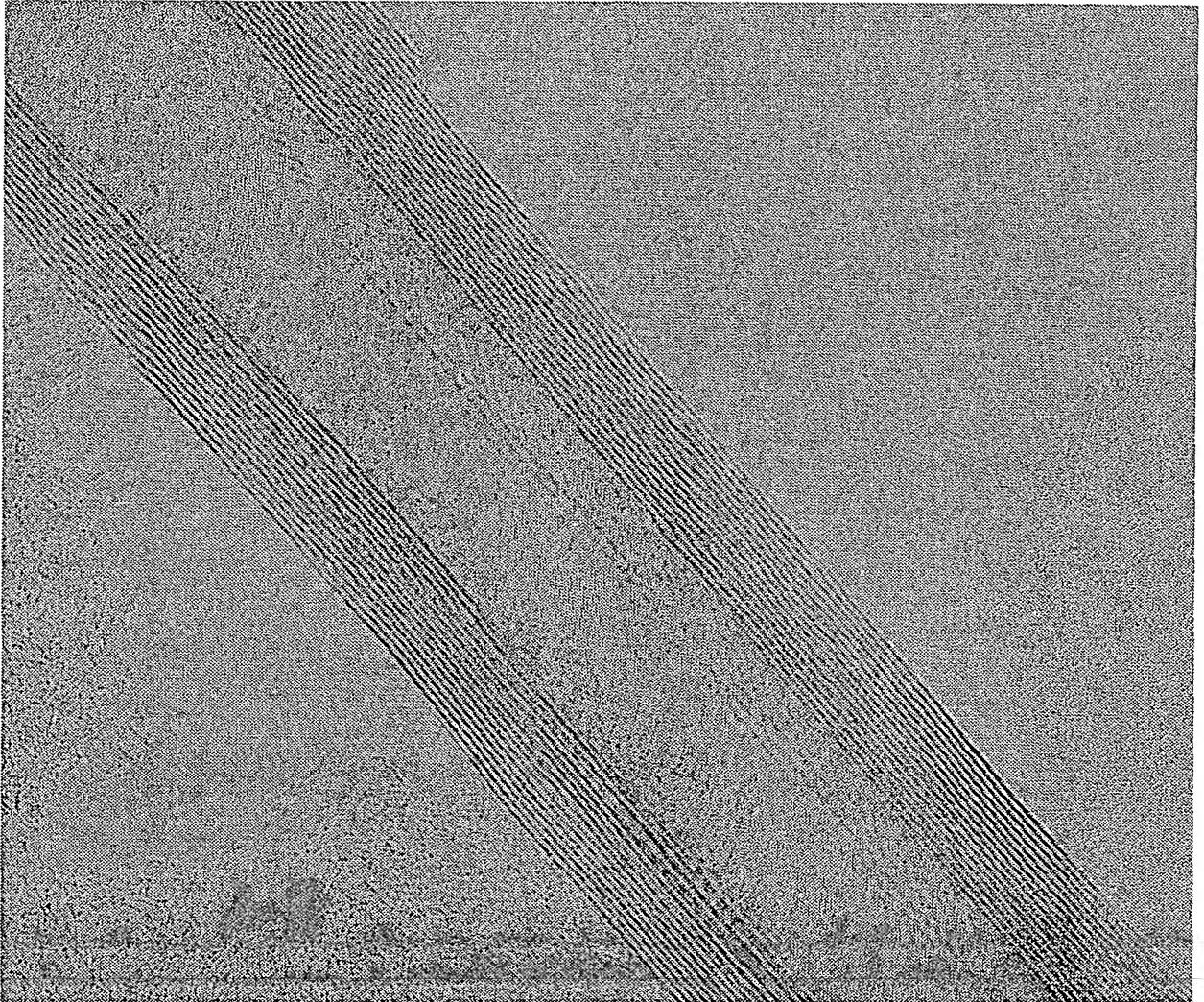


Figure 2

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Figure 3



INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C01B31/02 C04B14/38 C04B20/10 C09K15/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01B C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, INSPEC, COMPENDEX, CHEM ABS Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WHITBY, RAYMOND L. D. ET AL: "Tungsten disulphide sheathed carbon nanotubes" CHEMPHYSCHEM, vol. 2, no. 10, 15 October 2001 (2001-10-15), pages 620-623, XP002207104 the whole document	1-17, 24-26
X	WU G T ET AL: "Lithium insertion into CuO/carbon nanotubes" JOURNAL OF POWER SOURCES, vol. 75, no. 1, 1 September 1998 (1998-09-01), pages 175-179, XP002207103 ISSN: 0378-7753 the whole document	24-26



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

G document member of the same patent family

Date of the actual completion of the international search

26 July 2002

Date of mailing of the international search report

21/08/2002

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INTERNATIONAL SEARCH REPORT

PCT/GB 02/01963

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	SEEGER T ET AL: "SiO/sub x/-coating of carbon nanotubes at room temperature" CHEMICAL PHYSICS LETTERS, vol. 339, no. 1-2, 4 May 2001 (2001-05-04), pages 41-46, XP002207105 ISSN: 0009-2614 the whole document ---	24-26
X	SATISHKUMAR B C ET AL: "OXIDE NANOTUBES PREPARED USING CARBON NANOTUBES AS TEMPLATES" JOURNAL OF MATERIALS RESEARCH, NEW YORK, NY, US, vol. 12, no. 3, March 1997 (1997-03), pages 604-606, XP000974827 ISSN: 0884-2914 the whole document ---	24
X	MCCARTHY B ET AL: "Complex nano-assemblies of polymers and carbon nanotubes" EIGHT FORESIGHT CONFERENCE ON MOLECULAR NANOTECHNOLOGY, BETHESDA, MD, USA, 3-5 NOV. 2000, vol. 12, no. 3, pages 187-190, XP002206258 Nanotechnology, Sept. 2001, IOP Publishing, UK ISSN: 0957-4484 the whole document ---	26
P, X	MING ZHANG ET AL: "Synthesis of coaxial nanotubes: titanium oxide sheathed with silicon oxide" JOURNAL OF MATERIALS RESEARCH, MAY 2001, MATER. RES. SOC, USA, vol. 16, no. 5, pages 1408-1412, XP001007084 ISSN: 0884-2914 the whole document ---	26
X	PATENT ABSTRACTS OF JAPAN vol. 1997, no. 04, 30 April 1997 (1997-04-30) & JP 08 325195 A (NEC CORP), 10 December 1996 (1996-12-10) abstract --- -/--	26

INTERNATIONAL SEARCH REPORT

PCT/GB 02/01963

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>ZHANG Y ET AL: "Coaxial nanocable: silicon carbide and silicon oxide sheathed with boron nitride and carbon" SCIENCE, 14 AUG. 1998, AMERICAN ASSOC. ADV. SCI, USA, vol. 281, no. 5379, pages 973-975, XP002207106 ISSN: 0036-8075 the whole document</p> <p style="text-align: center;">----</p>	24-26
A	<p>MENG G W ET AL: "FORMATION OF BETA-SIC NANORODS WITH AMORPHOUS SiO₂ WRAPPING LAYERS" JOURNAL OF MATERIALS SCIENCE LETTERS, CHAPMAN AND HALL LTD. LONDON, GB, vol. 18, no. 15, 1 August 1999 (1999-08-01), pages 1255-1257, XP000849744 ISSN: 0261-8028</p> <p style="text-align: center;">----</p>	
A	<p>HSU W K ET AL: "C-MoS/sub 2/ and C-WS/sub 2/ nanocomposites" APPLIED PHYSICS LETTERS, 18 DEC. 2000, AIP, USA, vol. 77, no. 25, pages 4130-4132, XP002207107 ISSN: 0003-6951 cited in the application</p> <p style="text-align: center;">-----</p>	

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Information on patent family members

PCT/GB 02/01963

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
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